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### A R T I C L E S

# Selective Depositions on Polyelectrolyte Multilayers: Self-Assembled Monolayers of m-dPEG Acid as Molecular Template

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***Abstract:*** This paper describes the fabrication of self-assembled monolayer (SAM) patterns of m-d-poly-(ethylene glycol) (m-dPEG) acid molecules onto polyelectrolyte multilayers (PEMs). The patterned SAMs on PEMs were created by ionic interactions using microcontact printing ($\mu$CP) technique. The created m-dPEG acid monolayer patterns on PEMs act as resistive templates, and thus further depositions of consecutive poly(anion)/poly(cation) pairs of charged particles result in the formation of three-dimensional (3-D) patterned PEM films or selective particle depositions atop the original multilayer thin films. In this study, we illustrate nonlithographic methods of patterning and controlling 3-D PEM architectures and selective particle depositions. We investigated the effect of variables—the choice of solvent, concentration, pH, substrate pretreatment, and stamp contact times—on microcontact printing of m-dPEG acid molecules onto PEM films to determine the optimal conditions for these parameters to achieve efficient transfer of m-dPEG acid patterns onto PEMs. Among the variables, the pH of the m-dPEG acid ink solution played the most important role in the transfer efficiency of the patterns onto the multilayer films. The patterned films were characterized by optical microscopy and atomic force microscopy (AFM).

## Introduction

In recent years, organic thin films have attracted a great deal of attention from researchers in many fields due to their light weight, flexibility, ease of functionalization, and application. The ionic layer-by-layer (LBL) assembly technique, introduced by Decher in 1991,[1,2] is among the most exciting recent developments in this area. Films formed by electrostatic interactions between oppositely charged poly-ion species to create alternating layers of sequentially adsorbed poly-ions are called "polyelectrolyte multilayers" (PEMs). PEMs[2-4] are effective and economical approaches to depositing organic ultrathin organized films and have been further extended to functional polymers,[5,6] organic dyes,[7,8] colloids,[9-11] inorganic nanoparticles,[12,13] biomaterials,[14,15] and selective electroless metal depositions.[16]

The use of organic thin films in integrated optics, microelectronic devices, sensors, and optical memory devices requires a means of patterning and controlling the device architecture. Photolithography is the conventional patterning technique of choice, but lithographic techniques have limitations when applied to curved, nonplanar surfaces and involve multiple processing steps to create three-dimensional, functional, and multiple-level microstructures. Microcontact printing ($\mu$CP), introduced by Whitesides and co-workers,[17,18] provides a versatile method of chemically and molecularly patterning surfaces at the submicrometer scale. This technique is attractive due to its high fidelity and ease of duplication. $\mu$CP uses an elastomeric stamp to print a variety of molecules with submicrometer resolution and without the need for dust-free environments and harsh chemical treatments.[17-19] The stamp is coated with the desired molecules, and the molecules residing on the raised regions of the stamp are brought in contact with the host substrate when the stamp is printed. The transfer efficiency of the molecules from the stamp to the substrate depends on the relative strength of the interaction of these molecules with the substrate versus with the stamp.

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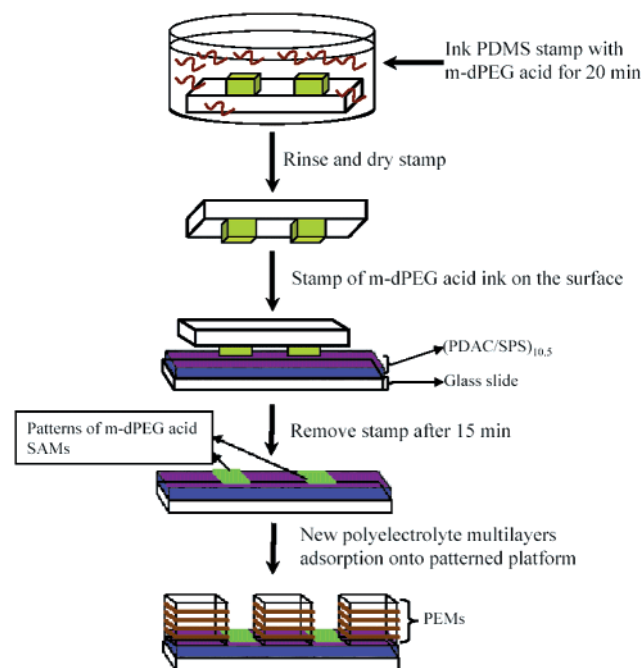**Scheme 1.** Illustration of Patterned SAMs on PEM[a]
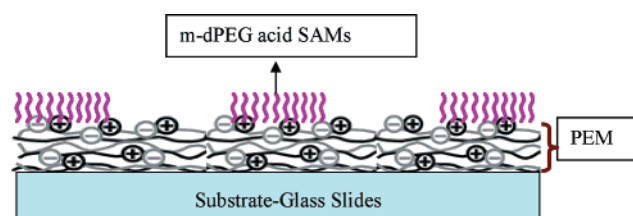


[a] The distance between the m-dPEG acid molecules is not drawn to scale, nor does it suggest the true nature of the packing density.

On the basis of the $\mu$CP and the LBL assembly techniques, Hammond and co-workers developed a polymer-on-polymer stamping (POPS) process using charged graft and diblock copolymers or polyelectrolytes as the ink.[20,21] They achieved selective deposition by introducing alternating regions of different chemical functionalities on a surface: one promoted adsorption and another effectively resisted adsorption of poly-ions onto the surface. We are exploring a similar approach where a m-dPEG molecule with an activated carboxylic acid group at the end can be stamped directly onto multilayer films to form patterned monolayers of SAMs, by carefully selecting their surface chemistry and taking advantage of electrostatic interaction between the top surface of the multilayer film and the stamped molecule. Chemical patterning of the topmost surface of the multilayer films provides a new nonlithographic approach to building and controlling device architectures.



**Mol. Wt.: 236.26**
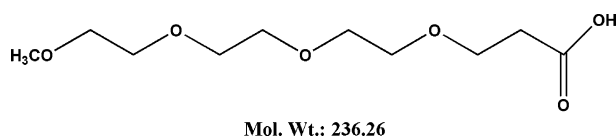
**Figure 1.** Chemical structure of PEG acid molecule (m-dPEG acid).

In this study, we describe the process of creating chemically patterned and physically structured surfaces by stamping molecules of m-dPEG acid (shown in Figure 1) activated with carboxylic acid at one end. Note that this is the first time patterned SAMs were created on PEMs (illustrated in Scheme 1), as opposed to on gold or silicon substrates. The activated carboxylate functional group ionically binds to the topmost positive surface of the PEM surfaces, and the other end (PEG units) resists the deposit of subsequent polymer (polyelectrolyte) layers. To create surfaces that can act as templates for selective layer-by-layer deposition, it is necessary to form surface regions that resist poly-ionic adsorption. To this end, poly(ethylene glycol) (PEG) and its oligomeric derivatives have thus far been the most effective materials to resist nonspecific adsorption of polyelectrolytes, charged particles, and proteins onto surfaces from aqueous solution.[22-27] PEG is a technologically important polymer used in numerous applications.[28-40] We capitalized

**Scheme 2.** Diagram Illustrating the Stamping Process of m-dPEG Acid on a PDAC/SPS Multilayer Platform



upon ionic interactions to deposit thin, uniform PEG self-assembled monolayer patterns atop PEM films and evaluated the variables that influence effective transfer of m-dPEG acid molecules onto the multilayer films as illustrated in Scheme 2. Our motivation for exploring the m-dPEG acid molecule as the molecular template for selective deposition is that it is a small molecule compared to other polymers with the PEG backbone used in other similar studies. As a result, it will provide us with better control in the pattern transfer onto the PEM surface. In addition, it can self-assemble to form monolayers on PEMs. The patterned SAMs on PEMs are possible like alkanethiol and alkanesilane SAMs that have been formed on gold or silicon wafers. We demonstrate that the PEG molecules create areas of selective adsorption on the multilayer films and can be used in the subsequent generation of 3-D microstructure films. The patterned films were characterized by optical microscopy and atomic force microscopy (AFM).

### Experimental Details

**Materials.** Sulfonated poly(styrene), sodium salt (SPS) ($M_w \approx$ 70 000), poly(diallyldimethylammonium chloride) (PDAC) ($M_w \approx$

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100 000–200 000) as a 20 wt % solution, and sodium chloride were purchased from Aldrich Chemical, Milwaukee, WI. The m-dPEG acid molecule ($M_w$ = 236) was obtained from Quanta Biodesign. Poly-(dimethylsiloxane) (PDMS) from the Sylgard 184 silicone elastomer kit (Dow Corning, Midland, MI) was used to prepare stamps. The fluorosilanes was purchased from Aldrich Chemical. These PDMS stamps were used for microcontact printing.[41] Glass slides (Corning Glass Works, Corning, NY), used for making the polyelectrolyte multilayer films, were cleaned using a Bransonic ultrasonic cleaner (Bransonic Ultrasonic Corporation, Danbury, CT). Carboxyfluorescein (6-CF), fluorescence dye, was purchased and used as received from Sigma. Carboxylated polystyrene latex particles (4 μm diameter), purchased from Polysciences, were used for colloidal adsorption study on m-dPEG self-assembled monolayer patterned polyelectrolyte templates.

**Preparation of Polyelectrolyte Multilayer Thin Films.** The strong polyelectrolytes SPS and PDAC were used to fabricate multilayer platforms using glass slides as the substrates. A Carl Zeiss slide stainer equipped with a custom-designed ultrasonic bath was connected to a computer to perform layer-by-layer assembly. Polyelectrolyte dipping solutions were prepared with DI water supplied by a Barnstead Nanopure-UV 4 stage purifier (Barnstead International Dubuque, Iowa), equipped with a UV source and final 0.2 μm filter. The concentration of SPS was 0.01 M and the concentration of PDAC solution was 0.02 M as based on the molecular repeat unit of the polymer, and all polyelectrolyte solutions contained 0.1 M NaCl. Solutions were filtered with a 0.45 μm Acrodisc syringe filter (Pall Corporation) to remove any particulates. The glass slides were cleaned with a dilute Lysol–water mixture in a sonicator. These slides were then dried under $N_2$ gas and were further cleaned using Harrick plasma cleaner (Harrick Scientific Corporation, Broading Ossining, NY) for 10 min at 0.15 Torr and 50 sccm flow of $O_2$ in a plasma chamber. To form the first bilayer, the slides were immersed for 20 min in a PDAC solution. Following two sets of 5 min rinse with agitation, the slides were subsequently placed in a SPS solution and allowed to deposit for 20 min. They were rinsed twice for 5 min each. The samples were cleaned for 3 min in an ultrasonic cleaning bath after depositing a layer of polycation/polyanion pair.[23] The sonication step removes weakly bounded polyelectrolytes on the substrate, forming uniform bilayers. This process was repeated to build multiple layers. All experiments were performed using 10 and a half bilayers (i.e., 21 layers), the topmost surface being PDAC (positive surface).

**Preparation of PDMS Stamps.** An elastomeric stamp is made by curing poly(dimethylsiloxane) (PDMS) on a microfabricated silicon master, which acts as a mold, to allow the surface topology of the stamp to form a negative replica of the master. The poly(dimethylsiloxane) (PDMS) stamps were made by pouring a 10:1 solution of elastomer and initiator over a prepared silicon master.[17] The silicon master was pretreated with fluorosilanes to facilitate the removal of the PDMS stamps from the silicon masters. The mixture was allowed to cure overnight at 60 °C. The masters were prepared in the Microsystems Technology Lab at MIT and consisted of features (parallel lines and circles) from 1 to 10 μm.

**Stamping of m-dPEG Acid.** The stamping conditions were varied to optimize the microcontact printing of the m-dPEG acid. PDMS stamps with and without plasma treatment were tested to stamp the ink. Ethanol/water mixtures were used as inks. Five solvents of this type were tried: pure ethanol, 75% ethanol, 50% ethanol, 25% ethanol, and pure water. The m-dPEG acid inks made with these solvents had concentrations of 10, 100, and 1000 μM. After solvent evaporation, the PDMS stamp was briefly dried under a $N_2$ stream and brought into contact with the substrate for 10–15 min at room temperature. Three different methods were used to ink the PDMS stamps: spin-inking,

cotton swab-inking, and dip-inking. For spin-inking the stamp was covered with ink and spun at 3000 rpm for 20 s. For the cotton swab-inking, a cotton swab was soaked in ink and rubbed over the surface of the stamp. The stamp was then dried with nitrogen. Using the dip-inking the stamp was soaked in ink, typically for 10 min, and dried with nitrogen.[42] In this study, the stamping times were varied systematically from a few seconds to an hour and the pH of the m-dPEG acid ink solution was varied from 2.0, 3.5, 4.5, to 6.5. Following the stamping process, the patterned surface was rinsed thoroughly with ethanol to remove unbound or loosely bound excess molecules to prepare self-assembled monolayer patterns. The stamped regions were designed to act as resists to adsorption as the oligoethylene glycol graft chains of PEG did.[20] In the procedure of creating complex 3-D microstructures, m-dPEG acid was stamped onto the PEM surface (PDAC surface) followed by sequential adsorption layer-by-layer deposition process to build additional patterned polyelectrolyte multilayers outside the stamped region.

**Characterization.** A Nikon Eclipse ME 600 optical microscope (Nikon, Melville, NY) was used to obtain dark field images of the m-dPEG acid patterns and the additional microfabricated PEMs. A Nikon Eclipse E 400 microscope was used to obtain the fluorescence images. The 6-carboxyfluorescein (6-CF) dye was used to visualize the m-dPEG SAM patterns on PEM following the stamping and rinsing processes. The dye was dissolved directly in 0.1 M NaOH; samples were imaged by dipping the substrates into the dye solution. The dye, which is negatively charged, preferentially stained the positively charged PDAC surface. The dyed regions appear green when viewed with the fluorescence optical microscope, using a FITC filter.[43] Images were captured with a digital camera and processed on a Pentium computer running camera software. After the polymers were stamped atop the multilayer platform, the topography of the stamped polyelectrolyte layer was observed by atomic force microscope (AFM) images. The AFM images were obtained with a Nanoscale IV controller (Digital Instruments, Santa Barbara, CA) equipped with tapping mode etched silicon probes and was operated in tapping mode.

## Results and Discussion

For the first time, we demonstrate that the creation of patterned SAMs on PEMs, using PEG acid molecules, can be achieved, as alkanethiol and alkanesilane molecules can form SAMs on gold or silicon wafers. In addition, we present approaches to fabricate complex 3-D microstructured functional films by incorporating the created m-dPEG SAMs on PEM surfaces. Using m-dPEG acid molecules with an activated carboxylic group facilitated the attachment of the m-dPEG acid molecules onto the topmost positive surface (PDAC) of the PEM surfaces (PDAC/SPS)$_{10.5}$ via ionic bonding. The SAM patterns of m-dPEG acid molecule act as a resistive template by resisting the addition of polyelectrolytes on the stamped regions. This helps to achieve complex 3-D microstructures atop the original set of PEMs by permitting selective building of subsequent PEMs outside the m-dPEG SAM patterns. The patterns were characterized using AFM, optical, and fluorescence microscopy.

**Patterning m-dPEG SAMs on Polyelectrolyte Multilayers.** In this study, we stamped m-dPEG acid molecule directly onto an outermost PDAC layer of a PDAC/SPS multilayer film to form patterned m-dPEG SAMs on PEMs. To enhance the transfer of the m-dPEG SAM patterns and the subsequent building of complex microstructures, the stamping process required optimized conditions.

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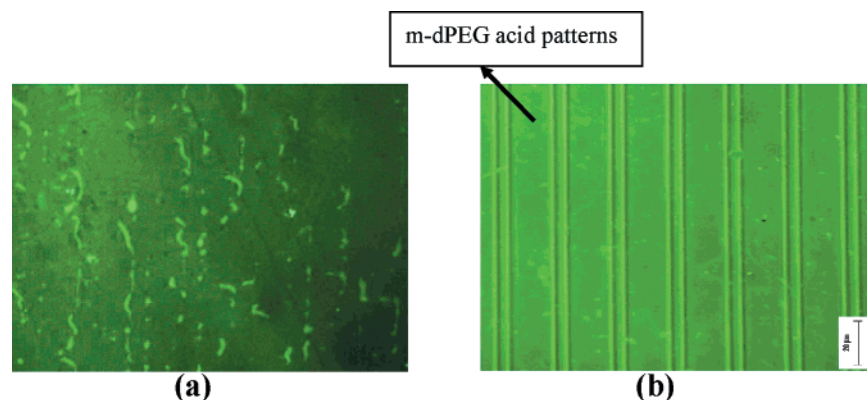
**Figure 2.** Defects occurring under nonoptimized stamping conditions: (a) Rimming occurs in areas of the stamp that were insufficiently inked (bare regions were also observed). (b) Streaking due to uneven application of the m-dPEG acid ink solution on the PDMS surface. All the images are fluorescence images, and the bars represent 20 $\mu$m.
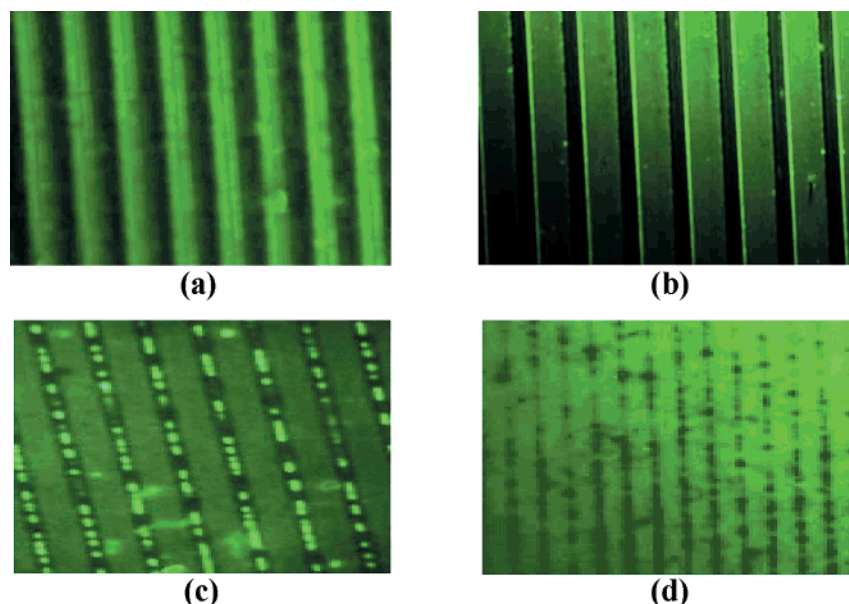


**Figure 3.** Effect of pH of m-dPEG acid "ink" on the patterns on top of (PDAC/SPS)$_{10.5}$: (a) pH = 6.5; (b) pH = 4.5; (c) pH = 3.5; (d) pH = 2.0. The green regions are the PEM films, and the black regions are the m-dPEG acid surface. The m-dPEG acid ink solution was evaluated at pH's of 2.0, 3.5, 4.5, and 6.5. When the pH is less than the p$K_a$ of the molecule (4.27 $\pm$ 0.20), the acid group does not completely ionize, leading to incomplete transfer of the patterns onto the multilayer films when compared to solutions with pH greater than the p$K_a$ value. At pH's of 4.5 and 6.5, uniform patterns are obtained due to the complete ionization of m-dPEG acid, resulting in stronger electrostatic attraction between the PDAC layer and the m-dPEG acid molecule. All the images are fluorescence images, and the bars represent 20 $\mu$m.

**Optimization of Stamping Process.** Figure 2 illustrates the various defects that occurred when m-dPEG acid molecules were stamped under nonoptimized conditions. For example, rimming (Figure 2a) or streaking (Figure 2b) in the stamped areas may arise when insufficiently or uneven application of the m-dPEG acid ink solution on the PDMS surface occurs. Determining the optimal conditions is important in achieving uniform and efficient transfer of m-dPEG acid molecules to form patterned SAMs on PEMs, which in turn affects the integrity of the device architecture for further applications. Various factors were evaluated in optimizing the stamping process, such as the plasma treatment of the PDMS stamps, the type and concentration of the solvents used in making the ink solution, and the contact times. The PDMS stamps were not treated with oxygen plasma since it was experimentally determined that untreated PDMS stamps resulted in more complete transfer of patterns when compared to the stamps treated with plasma. A solvent of 75% (v/v) ethanol/water gave the best results in terms of the effective transfer of the ink solution from the PDMS stamps onto the

surface and thus was used for the rest of the experiments. This optimal ethanol/water composition of the ink solvent corresponded to the previous results reported by the Hammond group.[21] Three different methods were used to ink the PDMS stamps: spin-inking, cotton swab-inking, and dip-inking. It was experimentally determined that the dip-inking method resulted in the most efficient transfer of the ink onto the PEM surface. The contact times were also varied from a few seconds to 30 min. The best pattern transfer resulted with a 15 min contact time. On the basis of the variables discussed above, the optimal stamping condition for m-dPEG acid was determined to be a solution of 100 $\mu$M of m-dPEG acid in a 75:25 ethanol/water mixture, stamped for 15 min using the dip-inking method of inking the PDMS stamps.

**Effect of pH.** Among the variables, the pH of the m-dPEG acid ink solution played the most important role in the transfer efficiency of the patterns onto the multilayer films. Figure 3 illustrates the effect of pH of the m-dPEG acid "ink" on the patterns of PEG SAM formed atop (PDAC/SPS)$_{10.5}$ using
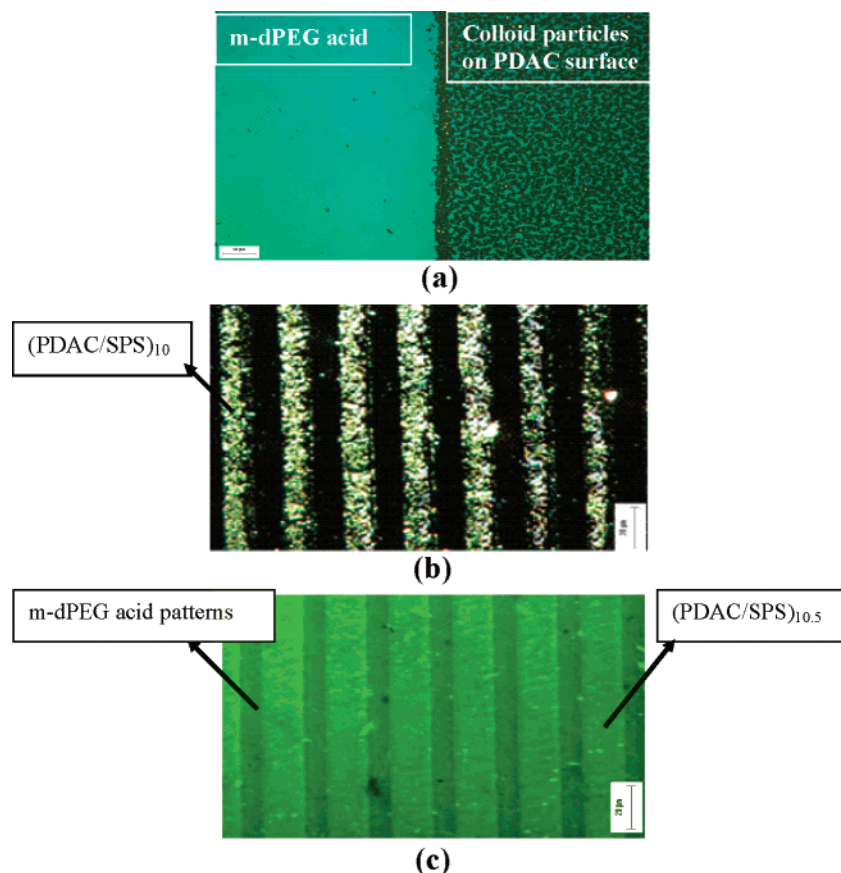
**Figure 4.** Optical microscope image of the m-dPEG acid patterns and dark field and fluorescent images of complex microstructures built atop the m-dPEG acid patterns. (a) m-dPEG acid was stamped on (PDAC/SPS)$_{10.5}$ as a resisting pattern using a blank stamp, and carboxylated polystyrene beads ($D = 4.1 \ \mu$m) were deposited on the outside regions of the m-dPEG self-assembled monolayer patterned surfaces. The left region, where there are no colloidal particles, is the m-dPEG acid region, while the right region with the colloidal particles is the PEM region. (b) Dark field optical images of complex microstructures formed by building PDAC/SPS atop the PEG patterns. The white regions are the PEM films, and the black regions are the m-dPEG acid surface. (c) Fluorescence images. The dark lines represent the m-dPEG acid regions, and the green regions represent the PEM surfaces.

fluorescent microscopy. The fluorescence dye used stained the PDAC surface due to ionic interaction. The presence of an alternating positive/m-dPEG SAM pattern is made clear by the presence of the negatively charged green dye on the positive PDAC regions.

The dark regions represent the m-dPEG acid patterns, which are not stained by the dye due to the lack of ionic interaction between the dye and m-dPEG acid surface. The carboxylic group of m-dPEG acid is responsible for the ionic interaction between m-dPEG SAM and the PDAC surface of the PEM. The extent of ionization of the acid group affects the strength of the ionic bond between the two ions and thus the extent of the pattern transfer. The ionization of m-dPEG acid, in turn, depends on the pH of the solution. It is apparent from Figure 3 that the micropattern transferred cleanly at pH 4.5 and 6.5, and in the case of pH values less than the p$K_a$ the transfer was not efficient.

### 3-D Microstructures Fabricated on PEMs

The fabrication of 3-D microstructures on PEMs using m-dPEG acid monolayer patterns as molecular resisting area is illustrated in Figure 4. PEG is known to be an effective polyelectrolyte that resists attachment of polymeric functional groups.[44] One of the goals in this work is to fabricate PEG self-assembled monolayer patterns onto PEMs by capitalizing upon ionic interactions at one end of the m-dPEG acid molecule and its resistance properties at the other end. As further proof for the existence of m-dPEG monolayer patterns on the PEM surface, negatively charged carboxylated polystyrene PS particles (diameter = 4 $\mu$m) were used. m-dPEG acid molecules were stamped on top of the (PDAC/SPS)$_{10.5}$ using a blank stamp (i.e., stamp with no patterns), as shown in Figure 4a, and the colloidal particles deposited selectively over the positive (PDAC/SPS)$_{10.5}$ surface (right) but not on the m-dPEG self-assembled monolayer regions (left). We were able to construct complex 3-D microstructures on top of the PEG monolayer patterned PEMs, for a variety of applications. After transferring m-dPEG monolayer patterns onto the PEM surfaces, subsequent depositing of PEMs resulted in 3-D heterostructures on the non-m-dPEG acid regions. Dark field optical microscopy and fluorescence microscopy were used to image the complex microstructures. Figure 4b illustrates dark field image of the PEMs built on top of the m-dPEG acid patterns. The black regions represent the m-dPEG acid surfaces, and the white regions represent the subsequent PEM films built on top of the m-dPEG SAM patterns. The white images of the patterned multilayers are due to the loopy and wavy deposits of the PEMs on the confined region (outside of the m-dPEG monolayer patterns). Figure 4c shows the fluorescence images of the microstructures. The green

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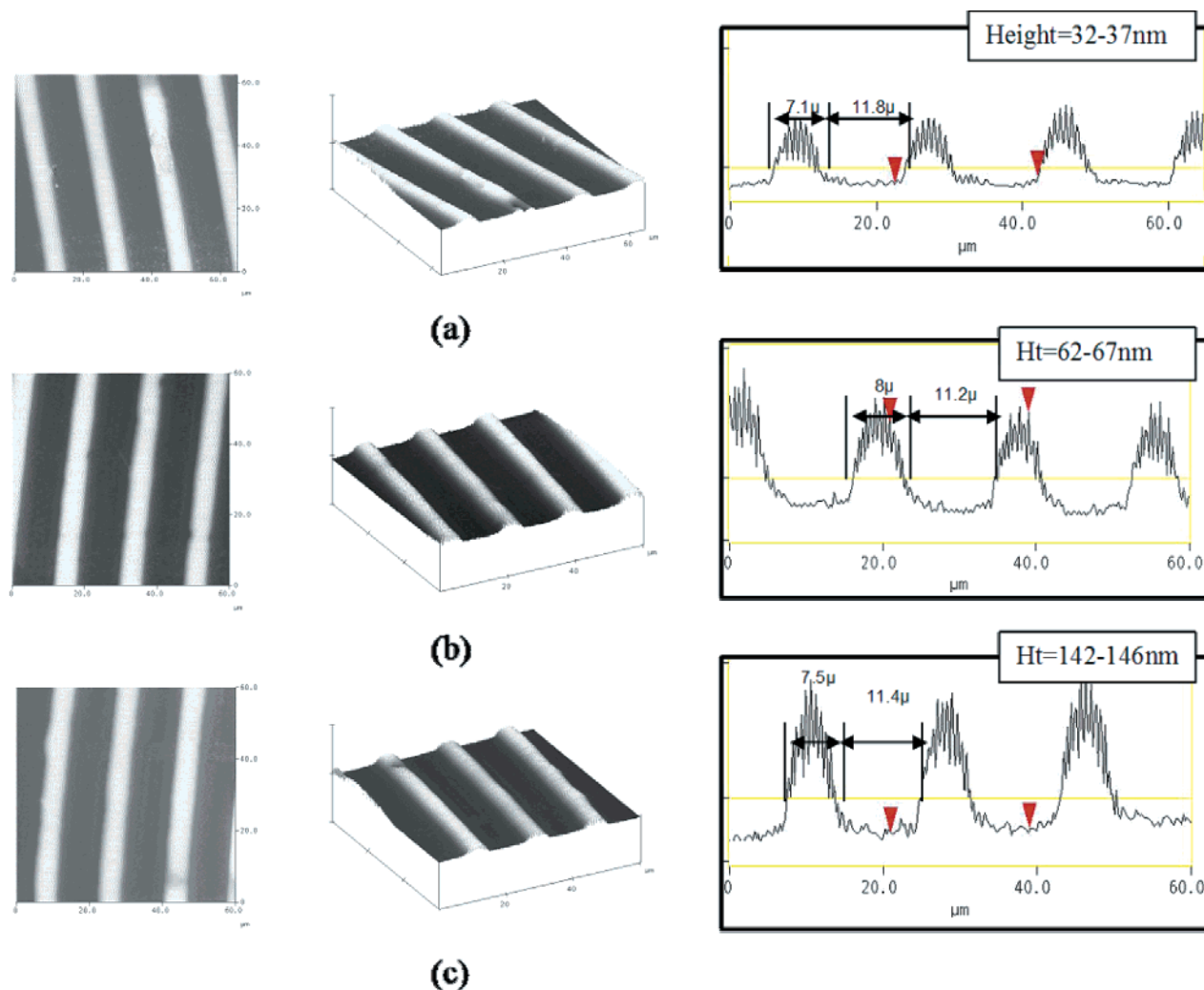
**Figure 5.** AFM images and topography of complex microstructures with different number of bilayers of PDAC/SPS built atop the m-dPEG acid patterns: (a) 10 bilayers, (b) 20 bilayers, and (c) 40 bilayers.

regions are the PEMs, and the dark regions are the m-dPEG monolayer regions. The stamped m-dPEG acid molecules are very small, with three ethylene glycol (EG) units. Due to the small chain length and the relative surface roughness of PEMs compared to gold or silicon wafers, we believe that these SAMs will be highly disorganized and loosely packed.

To provide further confirmation of the presence of the microstructures, Figure 5 illustrates the corresponding AFM images of the PDAC/SPS multilayer films built atop the stamped m-dPEG acid molecules. These images show the topography and the height variations of the PEM patterns deposited on the outside regions of the m-dPEG SAM patterns (i.e., the exposed PDAC area). The AFM images were taken for different number of layers of 3-D patterned PEMs, namely, 10, 20, and 40 bilayers. The height and the width of the patterns were determined using the AFM images. The height of the 3-D micropatterned PEMs (PDAC/SPS) linearly increased with the number of (PDAC/SPS) bilayers built on the outside region of the m-dPEG patterned SAM area. The heights of the 3-D microfabricated PEMs were determined by the AFM images and found to be 32−37 nm for 10 bilayers, 62−67 nm for 20 bilayers, and 142−146 nm for 40 bilayers. From these values, the average height of a pair of PDAC/SPS film was determined to be approximately 3.28−3.57 nm. This value agreed quite well

with the literature value of 3.4 nm for similar deposition conditions.[23]

## Conclusions

Micropatterning of the m-dPEG self-assembled monolayers has been demonstrated on PEM films as well as the building of subsequent 3-D micropatterned PEM structures on top of PEMs. Microfabrication of the functional and structured surfaces and interfaces were made using electrostatic interactions at the layered interfaces. In this work, the micropatterning of small PEG-modified molecules, m-dPEG acid on polymer surfaces (PEM films), was achieved purely by electrostatic interactions. As a result of small chain length and surface roughness of PEMs, we believe that the m-dPEG acid SAMs are disordered and loosely packed monolayers atop the PEM films. The stamping process was optimized by evaluating various conditions such as the inking method, the concentration, the contact times, and the need for plasma treatment of the stamps. Our results indicate that the strength of the ionic interactions between the acid and amine groups was the controlling variable during the stamping process. This variable was controlled mainly by the pH of the ink solution and the contact time. Strong polyelectrolytes such as PDAC and SPS are highly ionized over all or most of the pH range. On the other hand, the m-dPEG acid

molecule undergoes ionic interaction with PDAC when its acid group is completely ionized, which depends on the pH of the m-dPEG acid ink solution. Clean pattern transfer occurred for pH greater than the p$K_a$ value of m-dPEG acid. Patterning an initial set of multilayer films with a resistant molecule followed by subsequent deposition of multilayer films permitted the building of complex 3-D microstructures. These new patterned and structured surfaces have potential applications in micro-electronic devices and electro-optical and biochemical sensors. Finally, possibilities also exist in a variety of other areas that capitalize upon the formation of patterns and complex micro-structures, including biotechnological and biomedical applications.

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